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Electrical characteristics and surface topography of elastomeric nanocomposites based on multi-walled carbon nanotubes and poly(dimethylsiloxane)

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Abstract—This work presents the influence of the weight fraction of multi-walled carbon nanotubes (MWCNTs) in the poly(dimethylsiloxane) matrix on electrical insulating and morphological properties of the composite films. Atomic force microscopy surface topography maps showed good dispersion of MWCNTs within the polymer matrix without aggregates on the surface. Using of broadband dielectric spectroscopy measurements, it was found out that the percolation threshold of composite films lies in the MWCNTs concentration range of 0.5 - 1.5 wt. % in polymer matrix. For nanocomposites above to the percolation threshold, the impedance response showed a shift from conductive to dielectric-like behavior as frequency is increased. This global impedance response is attributed to the presence of conductive particles distributed in an insulating polymer matrix acting as a complex network of local resistors and capacitors.

Keywords—multi-walled carbon nanotubes, poly(dimethylsiloxane), polymer nanocomposites, electrical properties, AFM

I. INTRODUCTION

A composite material is defined as a material consisting of two or more different phases with a recognized interphase [1]. Nanocomposites containing fillers in the nanometer scale yield substantial improvements. Nanocomposites can be classified in terms of their matrices: metal-matrix, ceramic-matrix, and polymer-matrix. Polymer nanocomposites (PNCs) demonstrate excellent physicochemical, mechanical and electrical properties unavailable to individual components [2]. PNCs are twenty-first century high-performance materials used in a variety of advanced technologies: automotive, defense, aerospace, infrastructure, energy storage, environment remediation and biomedical medicine [3-6]. The extraordinary properties of carbon nanotubes (CNTs) in combination with the individual characteristics of polymers create truly versatile CNTs-polymer nanocomposites [7]. Polymeric insulators, in particular, poly(dimethylsiloxane) (PDMS), are known for their great electrical resistivity, light weight, hydrophobicity, high strength and low manufacturing cost [8]. The introduction of a small amount of multi-walled CNTs (MWCNTs) into an insulating polymeric matrix transforms MWCNTs-filled polymers in electrically conductive composites (high energy densities and low driving voltages) [9]. The electrical conductivity and percolation threshold of MWCNTs@PDMS nanocomposites depend on several factors, such as the dispersion state and dimensions of

carbon nanotubes, the alignment within the polymer matrix, and the composites processing method [10]. Such composites are used in anti-static packaging applications, as well as in the electronics, automotive and aerospace sectors [11]. In addition, atomic force microscopy (AFM) is a useful tool for the mapping of polymer composites because it can provide detailed information about material surface morphological properties and nanofillers distribution [12]. The purpose of this work is to study the electrical and surface morphological properties of PDMS composites filled with MWCNTs.

II. EXPERIMENTAL PROCEDURE

A. Materials

Pristine MWCNTs were used (average diameter 10-20 nm, about 15 layers and specific surface area of 160 m²/g), produced by the catalytic chemical vapour deposition method (CCVD) using pyrolysis of propylene on complex metal oxide catalysts [13]. PDMS (Sylgard 184 Silicone Elastomer Kit) consisting of a base elastomer (Part A, vinyl-terminated chains, viscosity of 5100 cSt) and a curing agent (Part B, comprising a platinum-containing compound as a curing catalyst) was purchased from Dow Corning, Germany. The ratio of Part A to Part B is 10:1. A low viscosity (10 cSt) silicone fluid with methyl group-terminated PDMS (MET) was bought from Sigma-Aldrich, Germany. Organic solvent n-hexane (high-performance liquid chromatography (HPLC) grade with >95 % purity) from Alfa Aesar (Kandel, Germany) was used to facilitate the dispersion of carbon nanotubes inside the PDMS matrix.

B. Preparation of MWCNTs@PDMS nanocomposites

Pristine MWCNTs were first dispersed in n-hexane and ultrasonicated for 10 min to obtain single CNTs dispersed in excess solvent solution. Then, Sylgard 184 (Part A) was added to the dispersion and ultrasonicated for 10 min. To obtain a homogeneous dispersion, low-viscosity (10 cSt) silicone fluid (MET) was added and ultrasonicated for 5 min. After n-hexane was evaporated from the dispersion using a hot plate at 70 °C, the cross-linker Sylgard 184 (Part B) was added and vigorously mixed. A vacuum pump was used to remove the bubbles remaining from the mixing process. The blend was cast in a mold and cured at 80 °C for 2 h in the oven. A range of weight percentage of the MWCNTs was considered from 0.25 to 2.5 wt. %. The neat PDMS was prepared using the

same fabrication technology. The flow diagram of the process is presented in the Fig. 1.

C. Characterization of MWCNTs@PDMS nanocomposites

The electrical properties of the neat PDMS and MWCNTs@PDMS nanocomposites in alternating current (AC) were investigated by the method of broadband dielectric spectroscopy (BDS) at room temperature (25 °C). For this, a Novocontrol Spectroscopy Alpha-A analyzer (Montabaur, Germany) with an applied voltage of 1 V_{rms} and a frequency range of 1 Hz to 1 MHz was used. BDS spectra were reported for the impedance modulus ($|Z_0|$) and the phase angle (θ_0). To perform the dielectric measurements, the samples were molded directly into rigid printed-circuit-board (PCB) sandwich structures. Two PCB boards, with a copper engraved electrode of 50 mm in diameter, were separated with two polymer spacers of 0.33 mm thickness each (Pacoplus 4500, Pacothane, Winchester, USA) and a central hole of 30.43 mm in diameter. When closed, sandwich structure contains the internal cavity of 30.43 mm in diameter x 0.66 mm in thickness that holds PDMS during reticulation at 80 °C. Metallized vias through the PCB boards extended the internal electrodes to the exterior of the sandwich structures for electrical measurements. The contribution of Pacoplus spacers for the insulating samples was taken into account. In the case of conductive ones, the contribution of Pacoplus spacers is reduced.

The surface morphology of the polymer nanocomposites was examined by atomic force microscopy (AFM) using a Bruker Multimode 8 apparatus. PeakForce Quantitative Nanomechanical (PF-QNM) was the mode of operation. Measurements were performed under ambient air using a RTESPA-150 antimony (n) doped silicon tip (resonance frequency $f_0 = 150$ kHz, spring constant $k = 6$ N.m⁻¹, tip radius = 8 nm). Nanoscope Analysis 1.8 software was used to analyze the obtained AFM images.

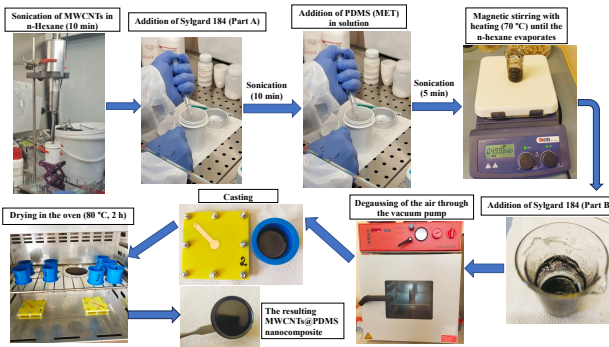


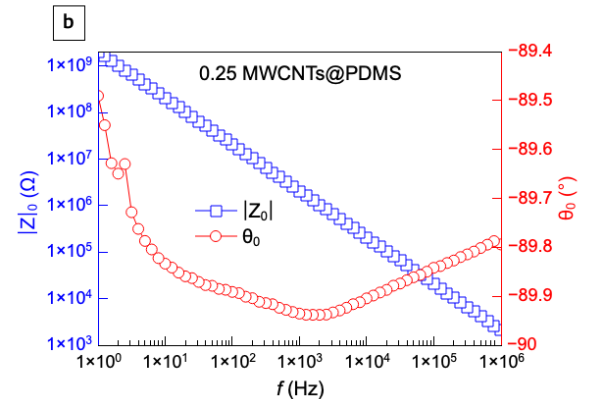
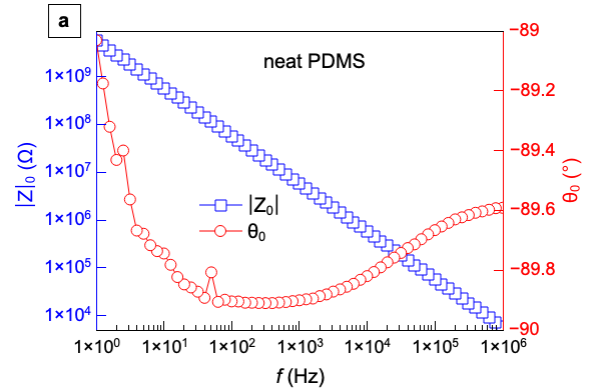
Fig. 1. Flow diagram of the polymer nanocomposite preparation.

III. RESULTS AND DISCUSSION

Representative BDS curves for neat PDMS and MWCNTs@PDMS nanocomposites at 0.25, 0.5, 1.5 and 2.5 wt. % are presented in Fig. 2. Fig. 2a shows that for the neat polymer, $|Z_0|$ decreases linearly with increasing frequency over the entire frequency range. For neat PDMS, as expected, only a capacitive behavior is observed. As shown in Fig. 2b and Fig. 2c, the behavior of polymer nanocomposites with 0.25 and 0.5 wt. % of MWCNTs is similar to the neat polymer one, with linearly decreasing values of $|Z_0|$ as f increases, and with values of θ_0 nearly constant and close to -90°. It can be argued that the mentioned MWCNTs@PDMS nanocomposites have not yet reached electrical percolation, so their electrical properties are determined by the properties of

the polymer. The behavior of the 1.5 MWCNTs@PDMS nanocomposite (Fig. 2d) is markedly different from neat PDMS and 0.5 MWCNTs@PDMS nanocomposite, suggesting that the percolation threshold lies between 0.5 and 1.5 wt. %. In the case of polymer nanocomposites with 1.5 and 2.5 wt. % of MWCNTs at frequencies below 10 kHz, the impedance remains almost constant and θ_0 remains close to zero (Fig. 2d and Fig. 2e). However, for frequencies of 10 kHz and higher, $|Z_0|$ decreases nonlinearly to $\sim 26 \Omega$ at 1 MHz (Fig. 1e). In the same frequency interval, θ_0 decreases toward more negative values, reaching -66° at 1 MHz. The dispersed conductive particles in an insulating matrix can be regarded as a distributed system of conductive and capacitive regions. When the particle inter-distance is large (in low-filler contents) the expected response is governed by the insulating matrix, hence a capacitive response in a broad frequency range. When the particles become closer (for high-filler contents) a shift from capacitive to conductive behavior in the low frequency spectrum will occur as close-range interactions increase. This has already been observed in polymer composites containing carbon nanostructures, particularly close to each other, which is the case when approaching the percolation threshold [14]. The response in a broad frequency range could be attributed to the presence of conductive particles dispersed in an insulating polymer matrix and to a local Maxwell-Wagner-Sillars polarization mechanism between particles [15].

According to the results discussed above, frequencies of 1 Hz and 10 kHz were selected for further comparison between the different analyzed composites. Fig. 3 presents the shift on the phase angle θ_0 as CNTs concentration increases. It shows that the percolation threshold, corresponding to the concentration above which the nanocomposite low-frequency dielectric response switches from a capacitive behavior to a resistive one belongs within the 0.5 to 1.5 wt. % concentration interval.



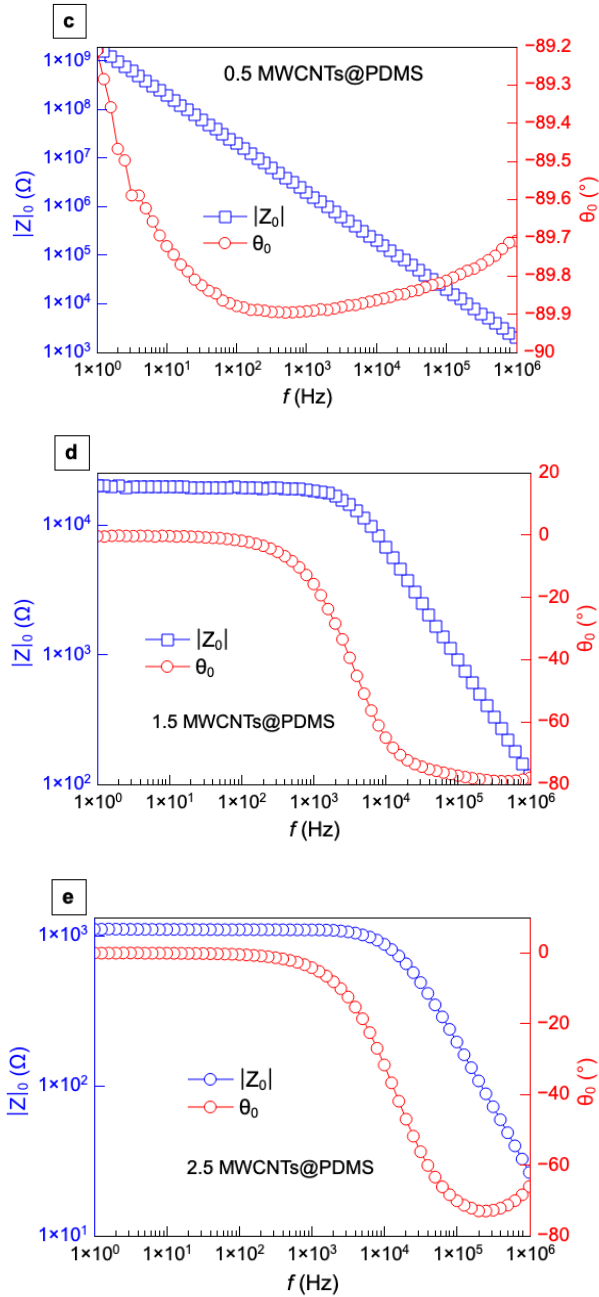


Fig. 2. Frequency response of the impedance of neat PDMS (a) and PDMS@MWCNTs (b-e) nanocomposites in the resistive configuration.

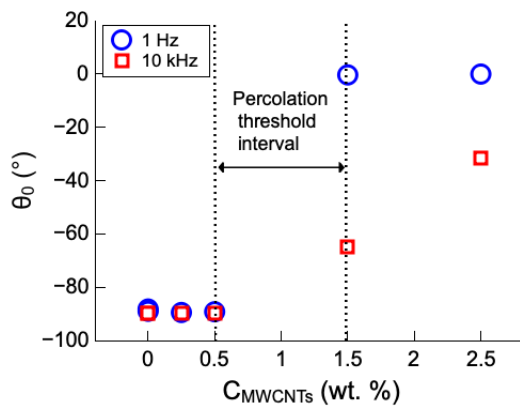


Fig. 3. Phase shift (θ_0) of the impedance response for the studied composites as a function of MWCNTs content, at 1 Hz and at 10 kHz.

The variation of AC conductivity frequency spectrum with weight fraction of MWCNTs is plotted in Fig. 4. AC conductivity is found to increase with the weight fraction as the frequency is varied from 1 Hz to 1 MHz. AC conductivity shows a steadily increasing behaviour at lower filler concentration (0.25, 0.5 wt. %) which is a pure dielectric response. At higher concentration (1.5, 2.5 wt. %), there is a plateau in the low-frequency range and exponential rise in the high-frequency range. According to the AC conductivity vs. pulsation relationship described by Jonscher [16] (eq. 1), the low-frequency plateau value corresponds to the direct current (DC) conductivity contribution, and the exponential rise with empirical A and n parameters corresponds to the dispersion contribution (A and n depending respectively on temperature and the specific material under study). Fig. 4 plots further illustrate the presence of a low frequency-range conductive behavior, due to percolation, for the nanocomposites with a weight fraction of MWCNTs between 0.5 wt. % and 1.5 wt. %.

$$\sigma_{AC}(\omega) = \sigma_{DC} + A\omega^n \quad (1)$$

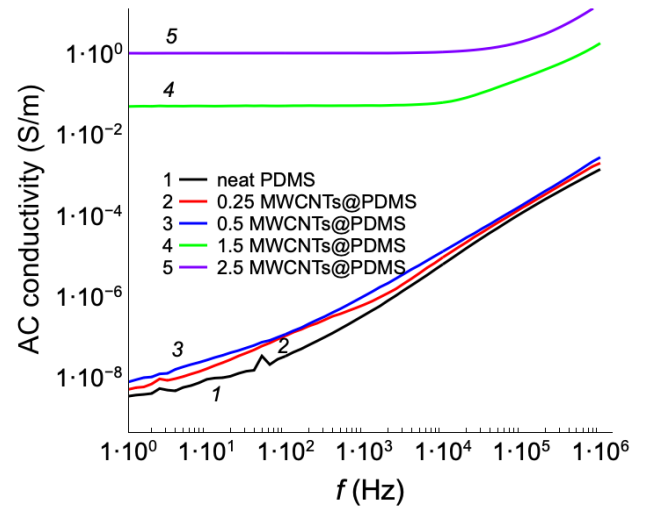


Fig. 4. Variation of AC electrical conductivity with frequency, for the different MWCNTs contents.

Thus, the graph in Fig. 4 demonstrates the presence of a low frequency-range resistive behavior due to percolation for the nanocomposites with a weight fraction of MWCNTs above 0.5 wt. %.

AFM surface topography measurements were performed on neat PDMS and MWCNTs@PDMS nanocomposites at 0.25 and 2.5 wt. % using the PF-QNM mode. Because of the PDMS matrix softness, a small peak force setpoint value was used (< 2 nN). Results are shown in Fig. 5 for $20 \mu\text{m} \times 20 \mu\text{m}$ topography maps. The corresponding arithmetic mean roughness (R_a) and root mean square roughness (R_q) were calculated and reported in Table I.

Surface topography maps of neat PDMS (Fig. 5a) and nanocomposites (Fig. 5b and Fig. 5c) are quite similar. The nanocomposites roughness values are lightly higher than the neat PDMS one: +9.3 % for 0.25 wt. % and +16.33 % for 2.5 wt. % MWCNTs@PDMS. The increase of the nanocomposite surface roughness results from the presence of MWCNTs within the matrix volume. However, there is no detection of MWCNTs aggregates on the surface since a small roughness increase was noticed between neat PDMS and nanocomposites.

The combined electrical and morphological results show the link between the dispersion state of fillers and the modification of the dielectric behavior and the percolation threshold of MWCNTs@PDMS nanocomposites.

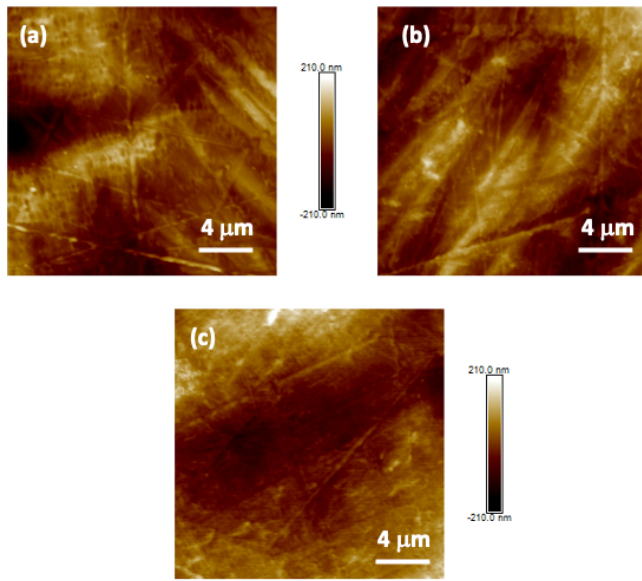


Fig. 5. 20 $\mu\text{m} \times 20 \mu\text{m}$ topography maps obtained in PF-QNM for (a) neat PDMS, (b) 0.25 wt. % and (c) 2.5 wt. % MWCNTs@PDMS.

TABLE I. SURFACE ROUGHNESS VALUES OF THE NEAT PDMS AND MWCNTs@PDMS NANOCOMPOSITES

Sample	R_a (nm)	R_q (nm)
neat PDMS	39.8	50.8
0.25 MWCNTs@PDMS	43.5	52.9
2.5 MWCNTs@PDMS	46.3	55.1

IV. CONCLUSIONS

The behavior presented by the dielectric response of the studied MWCNTs@PDMS nanocomposites indicates a transition from a capacitive to a resistive behavior depending on the particles content and shows the presence of a percolation threshold higher than 0.5 wt. % for 1 Hz. Topography results show a good dispersion of MWCNTs confirmed by the absence of aggregates on the samples surface. The joint electrical and morphological characterizations are necessary to confirm the link between the fillers dispersion state and the electrical behavior and percolation threshold of MWCNTs@PDMS nanocomposites. Further investigation on the volume dispersion of the MWCNTs and their alignment within the polymer matrix, as well as on the modeling of the nanocomposites global impedance response, will be interesting for future developments.

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